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Synthesis and Characterization of New Electroluminescent Materials of 1,3,4-Oxadiazole–1,2,3-Triazole Hybrids and 1,3,4-Oxadiazole–1,2,3-Triazole–Pyridine Derivatives

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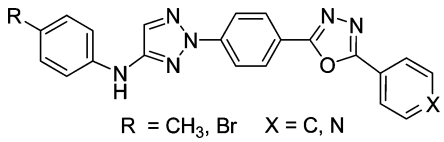
ABSTRACT: *New electroluminescent materials of 1,3,4-oxadiazole–1,2,3-triazole and 1,3,4-oxadiazole–1,2,3-triazole–pyridine hybrid derivatives were synthesized and characterized. Following spectroscopic studies and characterization of their electronic properties, 1,3,4-oxadiazole–1,2,3-triazole hybrids and 1,3,4-oxadiazole–1,2,3-triazole–pyridine derivatives were found to be potentially efficient blue electroluminescent materials.* © 2006 Wiley Periodicals, Inc. Heteroatom Chem 17:322–328, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20210



INTRODUCTION

1,3,4-Oxadiazole-based heterocyclic compounds [1] are the most widely studied classes of electron-injection and/or hole-blocking materials, mainly because of their electron deficiency, high-photoluminescence quantum yield, and good thermal and chemical stabilities [2]. We have developed and prepared a series of 1,3,4-oxadiazole-based heterocyclic hybrid derivatives as organic electroluminescent materials including 1,3,4-oxadiazole–pyrazole, 1,3,4-oxadiazole–pyridine–carbazole, 1,3,4-oxadiazole–1,-2,3-triazole, and 1,3,4-oxadiazole–triazolo-pyridinone derivatives [3]. Pyridine is a moderately electron-deficient π system, hybrids of pyridine and 1,3,4-oxadiazole could lead to increased

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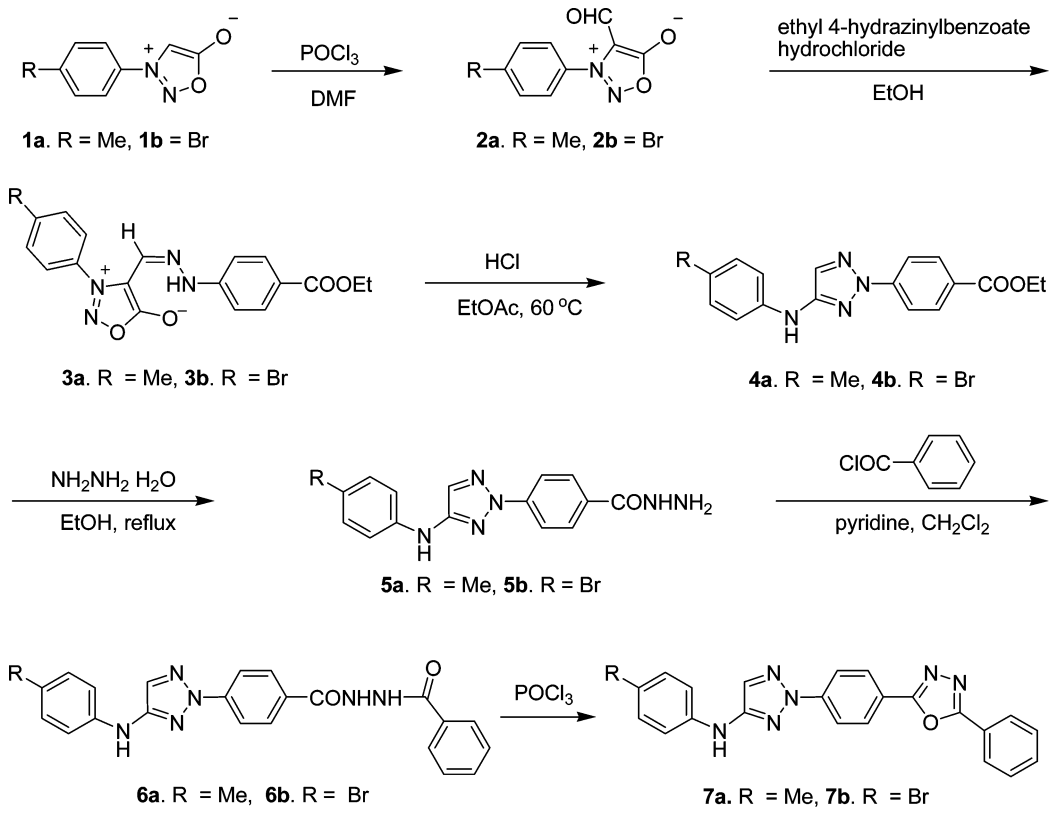
electron-injection ability [4]. In this paper, we focus on the synthesis and structure of the 1,2,3-triazole unit as incorporated into the 1,3,4-oxadiazole and explore the substituent effects of 2-substituted 1,3,4-oxadiazole with phenyl or pyridinyl groups. Following spectroscopic studies and cyclic voltammogram measurements, 1,3,4-oxadiazole–1,2,3-triazole hybrids and 1,3,4-oxadiazole–1,2,3-triazole–pyridine derivatives were found to be potentially highly efficient blue electroluminescent materials, and 1,3,4-oxadiazole–1,2,3-triazole–pyridine has a red-shift due to the substitution effect of pyridine moiety on the 2-position of 1,3,4-oxadiazole.

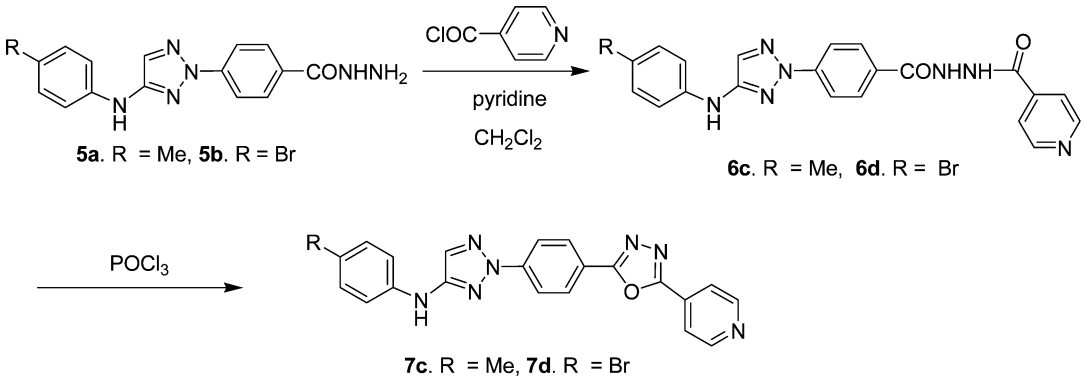
RESULTS AND DISCUSSION

New potential efficient blue electroluminescent materials of 1,3,4-oxadiazole–1,2,3-triazole **7a, 7b** and 1,3,4-oxadiazole–1,2,3-triazole–pyridine hybrid derivatives **7c, 7d** were synthesized and characterized for comparison. The sydnone starting materials **1a** and **1b** were prepared by the published procedure [5]. Sydnone compounds **1a** and **1b** were conveniently converted to 4-formyl-3-arylsydnone derivatives **2a, 2b** in a solution of $POCl_3$ and DMF by the Schmidt reaction in 70 and 60% yields, respectively [6]. Following the literature procedure [7], 3-(4-ethoxycarbonylbenzoyl)sydnone was dissolved in a solution of EtOAc with a few drops of HCl(aq) and stirred at room temperature to provide ethyl 4-hydrazinylbenzoate.

4-Formyl-3-arylsydnone derivatives **2a, 2b** were mixed with ethyl 4-hydrazinylbenzoate and stirred in the EtOH solution to carry out the imination, giving the corresponding products in good yields (**3a, 3b**, 80–83%). Compounds **3a** and **3b** were performed the acidic decomposition in the acidic EtOAc solution; the syndnones ring rearranged and the ring opening and decarboxylation proceeded sequentially to provide 4-arylamino-1,2,3-triazoles **4a, 4b** [5]. Treating 4-arylamino-1,2,3-triazoles **4a, 4b** with hydrazine monohydrate according to the published reports [8] afforded benzohydrazide compounds **5a** and **5b** in 80–83% yields. Condensation of benzohydrazide compounds with benzoyl chloride yielded the dihydrazide products **6a** and **6b**. We treated the raw materials **6a** and **6b** directly with $POCl_3$ [9] to obtain the cyclized 1,3,4-oxadiazol–1,2,3-triazole hybrids derivatives **7a, 7b**, which could be purified easily by column chromatography. The total synthesis route is shown in Scheme 1; structures were determined by high-field NMR spectroscopy and CHN analysis.



SCHEME 1



SCHEME 2

Benzohydrazide compounds **5a** and **5b** were treated with isonicotinoyl chloride hydrochloride to perform the condensation and yield the dihydrazide products (**6c** and **6d**) in 77–78% yields. Compounds **6c** and **6d** were directly reacted with $POCl_3$ [10] to obtain 1,3,4-oxadiazol–1,2,3-triazole–pyridine hybrids **7c, 7d**, which could be purified by column chromatography, their structures were determined by high-field NMR spectroscopy and CHN analysis (see Scheme 2).

UV–Vis spectra of 1,3,4-oxadiazol–1,2,3-triazole **7a, 7b** and 1,3,4-oxadiazol–1,2,3-triazole–pyridine derivatives **7c, 7d** were measured in THF, CH_2Cl_2, and $CHCl_3$ solutions. The λ_{max} values of **7a–7d** are in the range 346–362 nm in CH_2Cl_2 and $CHCl_3$ solutions and have a red-shift to 356–368 nm in THF solution due to the bathochromic shift in polar solvent effect (see Table 1) [11]. Compounds **7b** and **7d** exhibited a blue-shift (6–8 nm) due to the electron-withdrawing group (—Br) in the *para*-position on the *N*-phenyl group in the conjugation core (see Fig. 1).

Photoluminescence (PL) spectra of 1,3,4-oxadiazol derivatives **7a–7d** were shown in Table 1 and the λ_{max} values are in the range 409–469 nm in CH_2Cl_2, $CHCl_3$, and THF solutions. Similarly, bathochromic shifts (~20 nm) are also found on the emission spectra in CH_2Cl_2 and THF solutions. Compounds **7b** and **7d** including the electron-withdrawing group (R = Br) exhibit a blue-shift (~15 nm). The 1,3,4-oxadiazol–1,2,3-triazole–pyridine hybrids **7c, 7d** have a red-shift (~20 nm, see Fig. 2) and **7d** exhibits intense deep-blue fluorescence in THF solution (λ_{max}s of PL is 469 nm, see Fig. 3). The PL spectrum **7b** and **7d** of vacuum-evaporated films on quartz substrates, with a maximum at 435 and 475 nm, shows a red-shift (~20–30 nm), with respect to the solution spectrum as shown in Fig. 4.

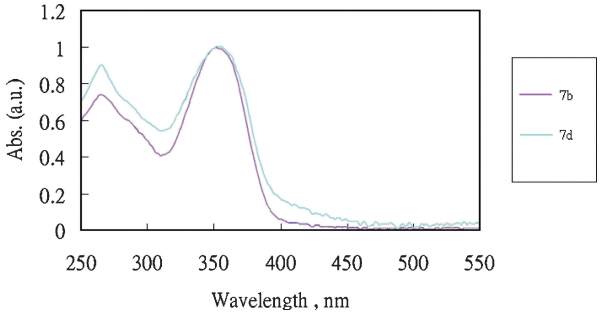


FIGURE 1 UV–Vis spectra of 1,3,4-oxadiazol–1,2,3-triazole derivatives with *p*-bromo-*N*-phenyl group **7b** and **7d** in THF solution.

The solution fluorescence quantum yields (Φ_f) of **7a–7d**, all of which fall in the range 0.68–0.74, were determined relative to that of 2-phenyl-5-(4-biphenyl)-1,3,4-oxadiazole in benzene ($\Phi_f = 0.80$)

TABLE 1 UV–Vis Absorption Maxima and Photoluminescence Peak Wavelength of 1,3,4-Oxadiazol–1,2,3-Triazole Derivatives **7a–7d**

		λ_{max} *(nm) of UV–Vis*			λ_{max} *(nm) of PL*			Φ_f[a]
Compound	*R*	$CHCl_3$	CH_2Cl_2	*THF*	$CHCl_3$	CH_2Cl_2	*THF*	*Benzene*
7a	Me	352	356	364	424	441	446	0.74
7b	Br	346	350	356	409	419	426	0.68
7c	Me	360	362	368	448	464	469	0.72
7d	Br	352	356	362	427	440	449	0.69

[a] Φ_f: fluorescence quantum efficiency, relative to 2-phenyl-5-(4-biphenyl)-1,3,4-oxadiazole in benzene ($\Phi_f = 0.8$).

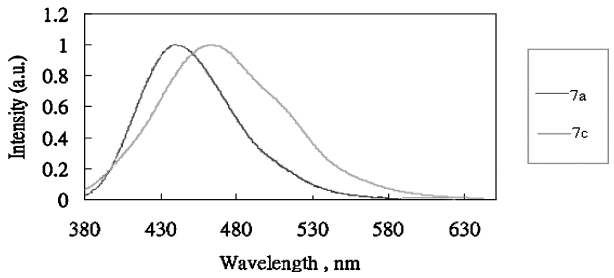


FIGURE 2 Normalized photoluminescence spectra of **7a** and **7c** in THF solution.

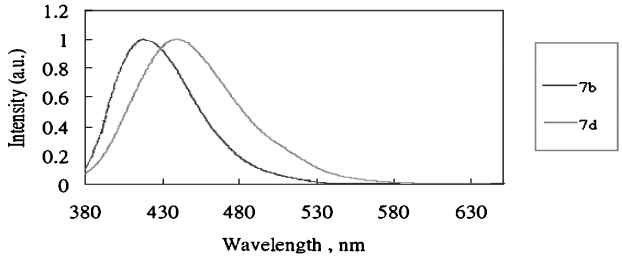


FIGURE 3 Normalized photoluminescence spectra of **7b** and **7d** in THF solution.

[12]. By comparison with their corresponding spectra in dilute solutions, the emission spectra of films of **7c** and **7d** are red-shifted by ~25 nm due to the substitution effect of pyridine on the main core of 1,3,4-oxadiazol–1,2,3-triazole–pyridine hybrids.

The electrochemical behavior of 1,3,4-oxadiazol–1,2,3-triazole derivatives (**7a–7d**) was investigated by cyclic voltammetry in solution. The measurements were carried out at a platinum electrode using CH_2Cl_2 containing 0.1 M of the supporting electrolyte, tetrabutylammonium hexafluorophosphate ($TBAPF_6$), in a three-electrode cell potentiostat assembly. The potential was measured against Ag/AgCl as a reference electrode and each measurement was calibrated with an internal standard, ferrocene/ferrocenium (Fc) redox system [13].

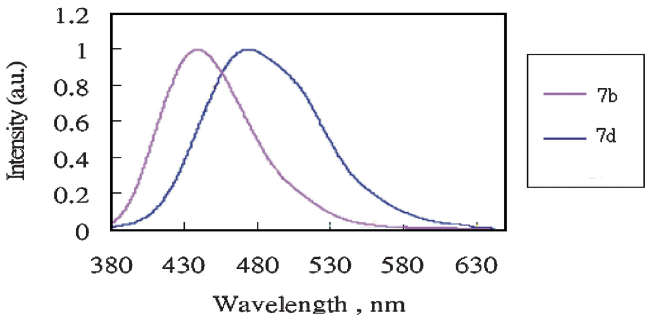


FIGURE 4 Normalized photoluminescence spectra of **7b** and **7d** in solid state (vacuum-evaporated film on quartz substrate).

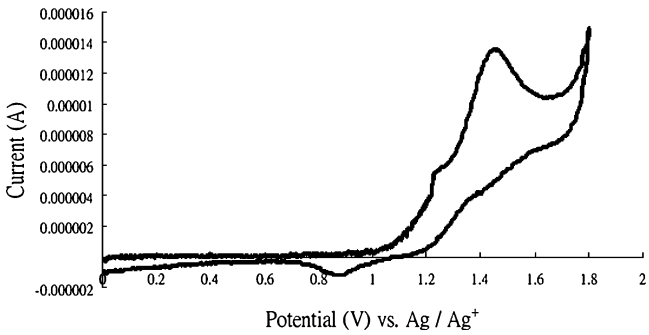


FIGURE 5 Cyclic voltammogram of **7d** in CH_2Cl_2 containing 0.1 M $TBAPF_6$ at a scan rate 50 mV/s.

The data were tabulated in Table 2. Upon the anodic sweep, **7a–7d** showed unclear reversible reduction processes. The bandgap energies of 1,3,4-oxadiazol–1,2,3-triazole derivatives (**7a–7d**) were estimated from the onset wavelength (λ_{onset}) of the UV–Vis absorption [4]. From the high-electron affinities, **7a–7d** are potentially electron-transporting, highly efficient blue electroluminescent materials. As an example, the cyclic voltammogram of **7d** is shown in Fig. 4. In the case of **7d**, the oxidation peak was estimated and the HOMO value is −5.68 eV with respect to Ag/AgCl (see Fig. 5).

TABLE 2 Electrochemical Properties of 1,3,4-Oxadiazol–1,2,3-Triazole Derivatives **7a–7d**

Compound	E^{a}_{onset} *(V)*	E'^{b}_{onset} *(V)*	$I_p^{c,f} = E_{HOMO}$ *(eV)*	$E_g^{d,f}$ *= bandgap energy (eV)*	$E_a^{e,f} = E_{LUMO}$ *(eV)*
7a	099	0.80	−5.60	3.17	−2.43
7b	1.10	0.91	−5.71	3.16	−2.55
7c	1.01	0.82	−5.62	3.10	−2.52
7d	1.07	0.88	−5.68	3.12	−2.56

[a] Measured vs. ferrocene/ferrocenium.
[b] $E'_{onset} = E_{onset} - 0.19$ eV (measured vs. Ag/AgCl).
[c] $I_p = -(E'_{onset} + 4.8)$.
[d] E_g: the bandgap energy estimated from the onset wavelength of UV–Vis absorption.
[e] $E_a = I_p + E'$.
[f] 1 eV = 96.5 kJ/mol.

CONCLUSION

We have successfully introduced 1,2,3-triazole and/or pyridine moieties into the core of 1,3,4-oxadiazole to provide a series of new potential blue electroluminescent materials. 1,3,4-Oxadiazole–1,2,3-triazole and 1,3,4-oxadiazole–1,2,3-triazole–pyridine hybrids are potentially highly efficient blue electroluminescent materials, by inducing 1,2,3-triazole and pyridine moieties to play an excellent assistant role in controlling the fundamental photolytic process. 1,3,4-Oxadiazole–1,2,3-triazole–pyridine have a red-shift due to the substituent effect of the pyridine moiety on the 2-position of 1,3,4-oxadiazole.

EXPERIMENTAL

Standard Procedure for Imination [5]

A solution of 4-formylsydnones (**2**, 6.0 g, 0.03 mol, 1.0 equiv.) was stirred in EtOH solution at room temperature. Ethyl 4-hydrazinylbenzoate hydrochloride (7.8 g, 0.035 mol, 1.1 equiv.) was added to the reaction mixture and stirred at room temperature for 3 h. After the reaction was completed, the reaction mixture was filtered and washed with cold EtOH. The wet cake was dried in a vacuum oven overnight and crystallized from CH_2Cl_2 to give 3-arylsydnonecarbaldehyde-4-aryl **3a, 3b** in 80–83% yields.

3-(4-Methylphenyl)-formylsydnone-p-ethoxycarbonylbenzoyl-hydrazone **3a**. The standard procedure was followed to prepare **3a** as white powder in 80% yield. ^{1}H NMR (DMSO-d_6, 200 MHz): δ 1.26 (t, $J = 7.0$ Hz, 3H, CH_3), 2.48 (s, 3H, CH_3), 4.24 (q, $J = 7.0$ Hz, 2H, CH_2), 6.70 (d, $J = 8.7$ Hz, 2H, Ar-H), 7.52 (s, 1H, CH), 7.54 (d, $J = 8.7$ Hz, 2H, Ar-H), 7.67–7.75 (m, 4H, Ar-H), 10.92 (s, 1H, NH).

3-(4-Bromophenyl)-formylsydnone-p-ethoxycarbonylbenzoyl-hydrazone **3b**. The standard procedure was followed to prepare **3b** as white powder in 83% yield. ^{1}H NMR (DMSO-d_6, 200 MHz): δ 1.26 (t, $J = 7.2$ Hz, 3H, CH_3), 4.20 (q, $J = 7.2$ Hz, 2H, CH_2), 6.59 (d, $J = 8.6$ Hz, 2H, Ar-H), 7.52 (s, 1H, CH), 7.72 (d, $J = 8.6$ Hz, 2H, Ar-H), 7.79 (d, $J = 8.6$ Hz, 2H, Ar-H), 10.97 (s, 1H, NH).

Standard Procedure for Preparation of 4-Aryamino-1,2,3-triazol-2-yl-benzoates **4a,b** *[5]*

A solution of 3-phenyl-formylsydnone-*p*-ethoxycarbon-ylbenzoyl-hydrazonecompounds (**3a** or **3b**, 3.0 g) and conc. HCl aqueous solution (3.0 mL) in EtOAc (30 mL) was stirred at 60°C. After the reaction was completed, the reaction mixture was concentrated and *i*-PrOH (15 mL) was added. The residues were concentrated again to remove the water. *i*-PrOH (15 mL) and activated carbon (~0.3 g) were added to the reaction mixture and stirred at room temperature for 1 h. The reaction mixture was filtered and cold water was added to precipitate the corresponding product (**4a** or **4b**). The product (**4a** or **4b**) was dried in a vacuum oven overnight to give the 4-aryamino-1,2,3-triazoles **4a, 4b** in 52–64% yields.

Ethyl 4-(4-(p-Tolylamino)-2H-1,2,3-triazol-2-yl)-benzoate **4a**. The standard procedure was followed to prepare **4a** as white powder in 64% yield. ^{1}H NMR (DMSO-d_6, 200 MHz): δ 1.28 (t, $J = 7.0$ Hz, 3H, CH_3), 2.41 (s, 3H, CH_3), 4.31 (q, $J = 7.0$ Hz, 2H, CH_2), 7.02 (d, $J = 8.6$ Hz, 2H, Ar-H), 7.47 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.80 (s, 1H, CH), 8.05–8.10 (m, 4H, Ar-H), 9.18 (s, 1H, NH).

Ethyl 4-(4-(4-Bromophenylamino)-2H-1,2,3-triazol-2-yl)benzoate **4b**. The standard procedure was followed to prepare **4b** as white powder in 52% yield. ^{1}H NMR (DMSO-d_6, 200 MHz): δ 1.30 (t, $J = 7.0$ Hz, 3H, CH_3), 4.28 (q, $J = 7.0$ Hz, 2H, CH_2), 7.08 (d, $J = 8.6$ Hz, 2H, Ar-H), 7.53 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.72 (s, 1H, CH), 8.04–8.12 (m, 4H, Ar-H), 9.36 (s, 1H, NH).

Standard Procedure for Preparation of 4-Aryamino-1,2,3-triazol-2-yl-benzohydrazides **5a,b** *[5]*

A solution of 4-aryamino-1,2,3-triazol-2-yl-benzoates **4a** or **4b** was stirred in EtOH (25 mL) and excess amount of hydrazine monohydrate (5.0 mL) solution. The reaction mixture was heated up to reflux. After the reaction was completed, the reaction mixture was concentrated and cold EtOAc (40 mL) was added to precipitate the corresponding products **5a** or **5b**. The products were filtered, washed, and dried in a vacuum oven overnight to give **5a** and **5b** in 72–75% yields.

4-(4-(p-Tolylamino)-2H-1,2,3-triazol-2-yl)benzohydrazide **5a**. The standard procedure was followed to prepare **5a** as white powder in 72% yield. ^{1}H NMR (DMSO-d_6, 200 MHz): δ 2.23 (s, 1H, CH_3), 4.51 (s, 2H, NH_2), 7.11 (d, $J = 8.6$ Hz, 2H, Ar-H), 7.38 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.67 (s, 1H, CH), 7.93–7.97 (m, 4H, Ar-H), 9.15 (s, 1H, NH), 9.82 (s, 1H, NH).

4-(4-(4-Bromophenylamino)-2H-1,2,3-triazol-2-yl)-benzohydrazide **5b**. The standard procedure was

followed to prepare **5b** as white powder in 71% yield. ^{1}H NMR (DMSO-d_6, 200 MHz): δ 4.51 (s, 2H, NH_2), 7.45 (d, $J = 8.6$ Hz, 4H, Ar-H), 7.72 (s, 1H, CH), 7.45 (d, $J = 8.6$ Hz, 4H, Ar-H), 9.47 (s, 1H, NH), 9.84 (s, 1H, NH).

Standard Procedure for Preparation of 4-Aryamino-1,2,3-triazol-2-yl-benzoic Acid Hydrazides **6a–6d** *[5]*

A solution of 4-aryamino-1,2,3-triazol-2-yl-benzohydrazides (**5a** or **5b**, 3.40 g, 1.0 equiv.) and pyridine (0.5 mL) were stirred in CH_2Cl_2 (15 mL) for 10 min. Benzoyl chloride or isonicotinoyl chloride hydrochloride (1.5 equiv.) was added to the reaction mixture and stirred at room temperature for 2–3 h. After the reaction was completed, the reaction mixture was filtered and washed with cold water (10 mL). The solid was dried in a vacuum oven overnight to give **6a–6d** in 77–84% yields.

Benzoic Acid N′-4-(4-p-Tolylamino-1,2,3-triazole-2-yl)benzoyl Hydrazide **6a**. The standard procedure was followed to prepare **6a** as white powder in 81% yield. ^{1}H NMR (DMSO-d_6, 200 MHz): δ 2.42 (s, 3H, CH_3), 7.12 (t, $J = 8.2$ Hz, 1H, Ar-H), 7.41 (d, $J = 8.0$ Hz, 2H, Ar-H), 7.50 (d, $J = 7.6$ Hz, 2H, Ar-H), 7.58 (d, $J = 7.4$ Hz, 2H, Ar-H), 7.71 (s, 1H, CH), 7.93 (d, $J = 7.6$ Hz, 2H, Ar-H), 8.00–8.10 (m, 4H, Ar-H), 9.19 (s, 1H, NH), 10.53 (s, 1H, NH), 10.58 (s, 1H, NH).

Benzoic Acid N′-4-(4-Bromophenylamino-1,2,3-triazole-2-yl)benzoyl Hydrazide **6b**. The standard procedure was followed to prepare **6b** as white powder in 84% yield. ^{1}H NMR (DMSO-d_6, 200 MHz): δ 7.42–7.56 (m, 9H, Ar-H), 7.76 (s, 1H, Ar-H), 7.93 (d, $J = 8.2$ Hz, 2H, Ar-H), 8.08 (d, $J = 8.2$ Hz, 2H, Ar-H), 9.52 (s, 1H, NH), 10.53 (s, 1H, NH), 10.59 (s, 1H, NH).

Isonicotinic Acid N′-4-(4-p-Tolylamino-1,2,3-triazole-2-yl)benzoyl Hydrazide **6c**. The standard procedure was followed to prepare **6c** as white powder in 77% yield. ^{1}H NMR (DMSO-d_6, 200 MHz): δ 2.25 (s, 3H, CH_3), 7.13 (d, $J = 8.2$ Hz, 2H, Ar-H), 7.41 (d, $J = 8.2$ Hz, 2H, Ar-H), 7.75 (s, 1H, CH), 7.83 (d, $J = 8.2$ Hz, 2H, Ar-H), 8.00–8.22 (m, 4H, Ar-H, Py-H), 8.79 (d, $J = 8.2$ Hz, 2H, Py-H), 9.18 (s, 1H, NH), 10.69 (s, 1H, NH), 10.85 (s, 1H, NH).

Isonicotinic Acid N′-4-[4-(-Bomophenylamino)-1,2,3-triazole-2-yl]benzoyl Hydrazide **6d**. The standard procedure was followed to prepare **6d** as white powder in 78% yield. ^{1}H NMR (DMSO-d_6, 200 MHz): δ 7.36–7.62 (m, 4H, Ar-H), 7.76 (s, 1H, CH), 7.83 (d, $J = 8.2$ Hz, 2H, Ar-H), 7.94–8.24 (m, 4H, Ar-H, Py-H), 8.79 (d, $J = 8.2$ Hz, 2H, Py-H), 9.50 (s, 1H, NH), 10.71 (s, 1H, NH), 10.85 (s, 1H, NH).

Standard Procedure for Preparation of 1,2,4-Oxadiazole–1,2,3-Triazole Hybrids **7a–7h** *[6]*

A solution of 4-aryamino-1,2,3-triazol-2-yl-benzoic acid hydracids (**6a–6h**, ~230 mg) in $POCl_3$ (10 mL) was stirred at 90°C for 10 h. After the reaction was completed, cold water (10 mL) was added to the reaction mixture and neutralized with NaOH aqueous solution (10 mL) to precipitate. The product was washed with cold water (5 mL), filtered, and dried in a vacuum oven overnight to give the desired product (**7a–7h**).

2-(4-(5-Phenyl-1,3,4-oxadiazol-2-yl)phenyl)-N-p-tolyl-2H-1,2,3-triazol-4-amine **7a**. The standard procedure was followed to prepare **7a** as white powder in 87% yield; mp 263–265°C. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 2.24 (s, 3H, CH_3), 7.14 (t, $J = 8.0$ Hz, 1H, Ar-H), 7.41 (d, $J = 8.2$ Hz, 2H, Ar-H), 7.50–7.74 (m, 4H, Ar-H), 7.73 (s, 1H, CH), 8.14 (d, $J = 8.2$ Hz, 2H, Ar-H), 8.27 (d, $J = 8.0$ Hz, 2H, Ar-H), 9.25 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 20.72, 116.29, 117.80, 120.80, 123.77, 126.80, 127.10, 128.75, 129.11, 129.86, 129.95, 132.47, 139.57, 141.78, 151.22, 164.02, 164.38; IR (KBr): 3334 (br, NH), 1611 (m, C=O), 1565, 1499, 1432 cm^{-1}; FABMS *m/z* (relative intensity): 397 (M + 2, 15), 396 (M + 1, 57), 396 (M^+, 41), 155 (19), 155 (30), 154 (100), 138 (41), 137 (79), 136 (76). Anal. Calcd for $C_{23}H_{18}N_6O$: C, 70.04; H, 4.60; N, 21.31. Found: C, 70.04; H, 4.56; N, 21.29.

N-(4-Bromophenyl)-2-(4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl)-2H-1,2,3-triazol-4-amine **7b**. The standard procedure was followed to prepare **7b** as white powder in 86% yield; mp 254–256°C. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 7.42–7.64 (m, 4H, Ar-H), 7.66–7.78 (m, 3H, Ar-H), 7.79 (s, 1H, CH), 8.15 (d, $J = 8.6$ Hz, 2H, Ar-H), 8.29 (d, $J = 8.6$ Hz, 2H, Ar-H), 9.59 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 111.44, 117.97, 118.18, 119.60, 123.74, 127.10, 128.73, 129.83, 132.17, 132.47, 141.35, 141.68, 145.32, 153.97, 164.41, 164.87; IR (KBr): 3310 (br, NH), 1601 (m, C=O), 1558, 1490, 1429 cm^{-1}; FABMS *m/z* (relative intensity): 461 (M + 2, 50), 460 (M + 1, 44), 459 (M^+, 51), 155 (24), 154 (100), 138 (28), 137 (59), 136 (63). Anal. Calcd for $C_{22}H_{15}BrN_6O$: C, 57.53; H, 3.29; N, 18.30. Found: C, 57.49; H, 3.30; N, 18.33.

2-(4-(5-(Pyridin-4-yl)-1,3,4-oxadiazol-2-yl)phenyl)-N-p-tolyl-2H-1,2,3-triazol-4-amine **7c**. The standard procedure was followed to prepare **7c** as white powder in 82% yield; mp 269–271°C. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 2.47 (s, 3H, CH_3), 7.10 (d, $J = 8.2$ Hz, 2H, Ar-H), 7.42 (d, $J = 8.2$ Hz, 2H, Ar-H), 7.74 (s, 1H, CH), 8.02 (d, $J = 8.2$ Hz, 2H, Ar-H), 8.02 (d, $J = 8.2$ Hz, 2H, Ar-H), 8.12 (d, $J = 8.4$ Hz, 2H, Py-H), 8.26 (d, $J = 8.2$ Hz, 2H, Ar-H), 8.84 (d, $J = 8.4$ Hz, 2H, Py-H), 9.45 (s, 1H, NH);^{13}C NMR (DMSO-d_6, 75 MHz): δ 20.72, 116.30, 117.74, 120.31, 120.65, 127.01, 128.98, 129.86, 132.31, 132.83, 139.59, 142.01, 150.62, 151.34, 162.86, 164.80; IR (KBr): 3434 (br, NH), 1610 (m, C=O), 1566, 1518, 1495, 1432 cm^{-1}; FABMS *m/z* (relative intensity): 397 (M + 2, 5), 396 (M + 1, 18), 395 (M^+, 10), 155 (23), 155 (23), 154 (100), 138 (35), 137 (60), 136 (96). Anal. Calcd for $C_{22}H_{17}N_7O$: C, 66.83; H, 4.33; N, 24.80. Found: C, 66.78; H, 4.34; N, 24.83.

N-(4-Bromophenyl)-2-(4-(5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)phenyl)-2H-1,2,3-triazol-4-amine **7d**. The standard procedure was followed to prepare **7d** as white powder in 84% yield; mp 287–289°C. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 7.34–7.64 (m, 4H, Ar-H), 7.76 (s, 1H, CH), 8.03 (d, $J = 8.2$ Hz, 2H, Ar-H), 8.12 (d, $J = 8.8$ Hz, 2H, Py-H), 8.26 (d, $J = 8.8$ Hz, 2H, Ar-H), 8.84 (d, $J = 8.8$ Hz, 2H, Py-H), 9.62 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 111.44, 118.19, 119.37, 120.63, 127.14, 128.96, 130.82, 132.13, 132.83, 141.32, 141.90, 150.62, 151.33, 162.89, 164.75; IR (KBr): 3428 (br, NH), 1606 (m, C=O), 1556, 1489, 1415 cm^{-1}; FABMS *m/z* (relative intensity): 462 (M + 2, 7), 461 (M + 1, 28), 460 (M^+, 29), 155 (25), 154 (100), 138 (33), 137 (55), 136 (80). Anal. Calcd for $C_{21}H_{14}BrN_7O$: C, 54.80; H, 3.07; N, 21.30. Found: C, 54.88; H, 3.03; N, 21.25.

REFERENCES

[1] For reports of 1,3,4-oxadiazole–heterocycle hybrids, see: (a) Wang, C.; Jung, G..-Y.; Batsanov, A. S.; Bryce, M. R.; Petty, M. C. J Mater Chem 2002, 12, 173; (b) Guan, M.; Bian, Z. Q.; Zhou, F. Y.; Li, Z. J.; Li, Z. J.; Haung, C. H. Chem Commun 2003, 2708; (c) Zhang, Q.; Chen, J.; Cheng, Y.; Wang, L.; Ma, D.; Jing, X.; Wang, F. J Mater Chem 2004, 14, 895; (d) Chien, Y.; Wong, K.; Chou, P.; Cheng, Y. Chem Commun 2002, 2874.

[2] For reviews, see: (a) Kraft, A. C.; Holmes, A. B. Angew Chem Int Ed Engl 1998, 37, 402; (b) Segura, J. L. Acta Polym 1998, 49, 319; (c) Thelakkat, M.; Schidt, H.-W. Polym Adv Technol 1998, 9, 429; (d) Mitschke, U.; Bäuerle, P. J. Mater Chem 2000, 10, 1471.

[3] The present results were submitted for publication.

[4] Wang, C.; Jung, G.-Y.; Hua, Y.; Pearson, C.; Bryce, M. R.; Petty, M. C.; Batsanov, A. S.; Goeta, A. R.; Howard, J. A. Chem Mater 2001, 13, 1167.

[5] (a) Yeh, M.-Y.; Tien, H.-J.; Huang, L.-Y.; Chen, M.-H. J Chin Chem Soc 1983, 30, 29; (b) Thoman, C. J.; Voaden, D. J.; Hunsberger, I. M. J Org Chem 1964, 29, 2044; (c) Dallacker, F.; Kern, J. Ber 1966, 99, 3830; (d) Kuo, W.-F.; Lin, I.-T.; Sun, S.-W.; Yeh, M.-Y. J Chin Chem Soc 2001, 48, 769.

[6] Thelakkat, M.; Schmidt, H.-W. Adv Mater 1998, 10, 219.

[7] Masuda, K.; Kikuchi, K. Imajo, Y. Chem Abstr 1973, 78, 124597e.

[8] Eade, A.; Earl, J. C. J Chem Soc 1946, 591.

[9] Shinohafa, H.; Ichimiya, Y.; Yoshimura, T.; Okawara, M. Chem Abstr 1960, 54, 22636i.

[10] Wang, C.; Jung, G.-Y.; Hua, Y.; Pearson, C.; Bryce, M. R.; Petty, M. C.; Batsanov, A. S.; Goeta, A. R.; Howard, J. A. Chem Mater 2001, 13, 1167.

[11] Hwu, J. R.; Chuang, K.-S.; Chuang, S. H.; Tsay, S.-C. Org Lett 2005, 7, 1545.

[12] Demas, J. N.; Crosby, G. A. J Phys Chem 1971, 75, 991.

[13] Wu, F.-I.; Shu, C.-F.; Chien, C.-H.; Tao, Y.-T. Synth Met 2005, 148, 133.